

Supporting Information

## Room temperature ionic liquid assisted synthesis of ultra-stable Au nanoparticles via a modified Brust-Schiffrin method

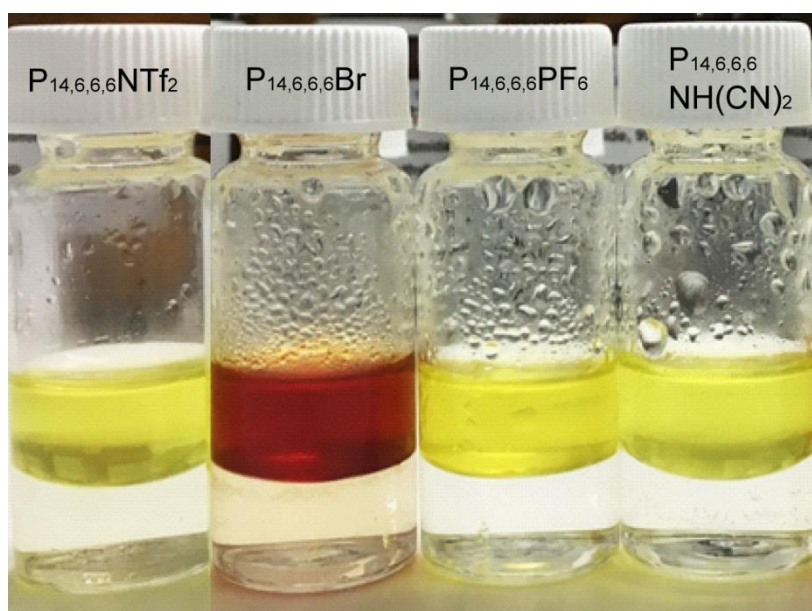
Limin Wu, Jingfang Zhou\* and Haolan Xu\*

RTIL	Miscible with toluene	Extraction of AuCl <sub>4</sub> <sup>-</sup>	Other
P <sub>14,6,6,6</sub> NTf <sub>2</sub>	√	√	
P <sub>14,6,6,6</sub> Cl	√	-	Turbid mixture
P <sub>14,6,6,6</sub> Br	√	√	
P <sub>14,6,6,6</sub> NH(CN) <sub>2</sub>	√	√	
P <sub>14,6,6,6</sub> PF <sub>6</sub>	√	√	
P <sub>8,8,8,8</sub> Br	√	√	
P <sub>14,4,4,4</sub> Cl	√	-	Turbid mixture
P <sub>4,4,4,4</sub> Cl	√	×	
N <sub>8,8,8,1</sub> NTf <sub>2</sub>	√	√	
N <sub>4,1,1,1</sub> NTf <sub>2</sub>	×	×	
EMIM NTf <sub>2</sub>	×	-	
HMIM NTf <sub>2</sub>	×	-	
HMIM PF <sub>6</sub>	×	-	
MPPiper NTf <sub>2</sub>	×	-	
MPPyro NTf <sub>2</sub>	×	-	
PPri NTf <sub>2</sub>	×	-	

**Table S1.** List of the sixteen RTILs and the corresponding physical and chemical properties.

√: positive; ×: negative; -: data not available

Name	Abbreviation	Structure
Trihexyltetradecylphosphonium bis (trifluoromethylsulfonyl) imide	$P_{14,6,6,6}$ NTf <sub>2</sub>	$\begin{array}{c} (\text{CH}_2)_5\text{CH}_3 \\   \\ \text{H}_3\text{C}(\text{H}_2\text{C})_5-\text{P}^+-\text{(CH}_2\text{)}_{13}\text{CH}_3 \\   \\ (\text{CH}_2)_5\text{CH}_3 \\ \text{F}_3\text{CO}_2\text{S}^-\text{N}^-\text{SO}_2\text{CF}_3 \end{array}$
Trihexyltetradecylphosphonium bromide	$P_{14,6,6,6}$ Br	$\begin{array}{c} (\text{CH}_2)_5\text{CH}_3 \\   \\ \text{H}_3\text{C}(\text{H}_2\text{C})_5-\text{P}^+-\text{(CH}_2\text{)}_{13}\text{CH}_3 \\   \\ (\text{CH}_2)_5\text{CH}_3 \quad \text{Br}^- \end{array}$
Trihexyltetradecylphosphonium hexafluorophosphate	$P_{14,6,6,6}$ PF <sub>6</sub>	$\begin{array}{c} (\text{CH}_2)_5\text{CH}_3 \\   \\ \text{H}_3\text{C}(\text{H}_2\text{C})_5-\text{P}^+-\text{(CH}_2\text{)}_{13}\text{CH}_3 \\   \\ (\text{CH}_2)_5\text{CH}_3 \quad \text{PF}_6^- \end{array}$
Trihexyltetradecylphosphonium dicyanamide	$P_{14,6,6,6}$ NH(CN) <sub>2</sub>	$\begin{array}{c} (\text{CH}_2)_5\text{CH}_3 \\   \\ \text{H}_3\text{C}(\text{H}_2\text{C})_5-\text{P}^+-\text{(CH}_2\text{)}_{13}\text{CH}_3 \\   \\ (\text{CH}_2)_5\text{CH}_3 \quad \text{NC}^-\text{N}^-\text{CN} \end{array}$

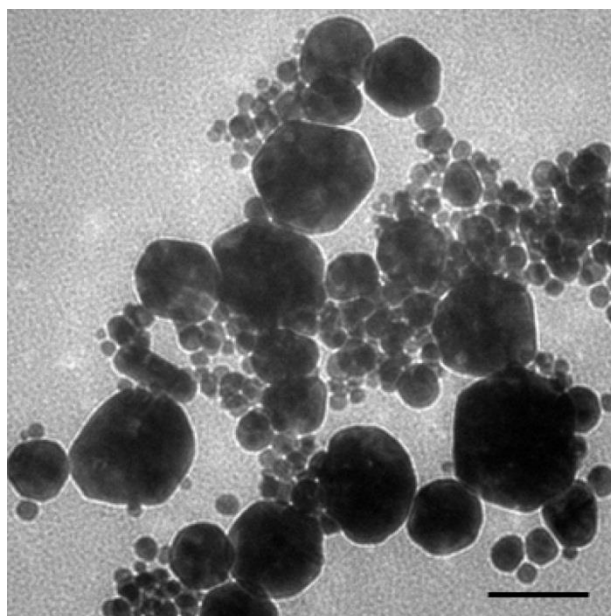


**Fig. S1** List of the selected RTILs and the digital photographs of water-RTILs after Au ion extraction, the upper layers are RTILs containing extracted Au ion.

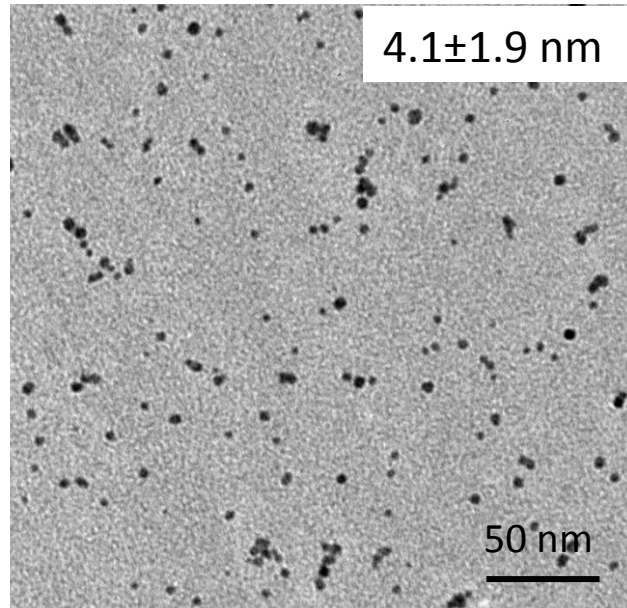


<b>Ionic Liquid</b>	Au@P <sub>14,6,6,6</sub> NTf <sub>2</sub>	Au@P <sub>14,6,6,6</sub> Br	Au@P <sub>14,6,6,6</sub> PF <sub>6</sub>	Au@P <sub>14,6,6,6</sub> NH(CN) <sub>2</sub>
<b>Average Zeta Size(d. nm)</b>	6.5±1.8	6.0±1.2	7.0±1.8	10.1±2.2

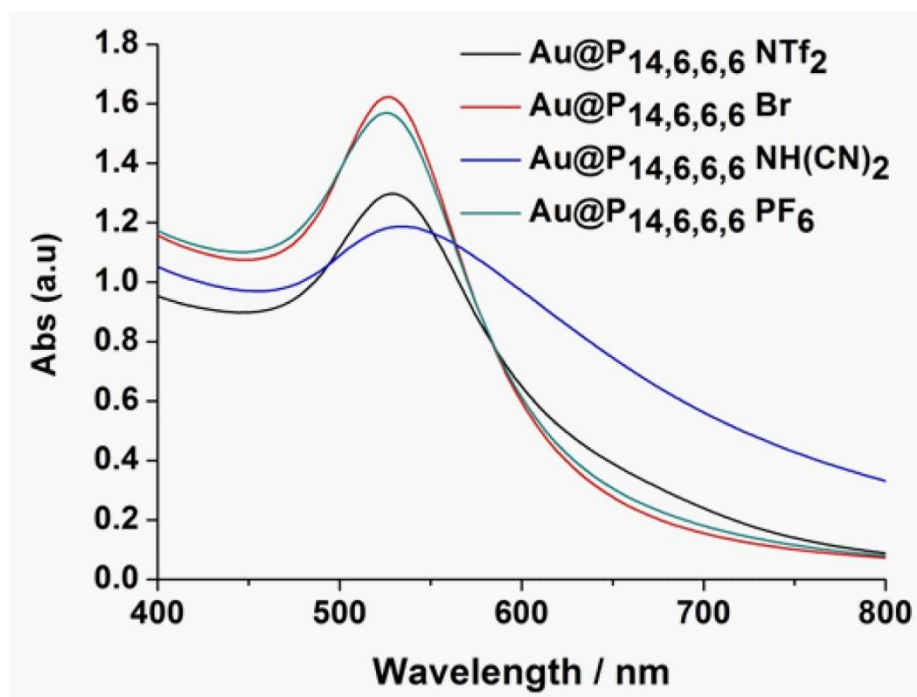
**Fig. S2** Digital photographs and DLS size of the Au@P<sub>14,6,6,6</sub>NTf<sub>2</sub>, Au@P<sub>14,6,6,6</sub>Br, Au@P<sub>14,6,6,6</sub>PF<sub>6</sub>, and Au@P<sub>14,6,6,6</sub>NH(CN)<sub>2</sub> NPs (from left to right).



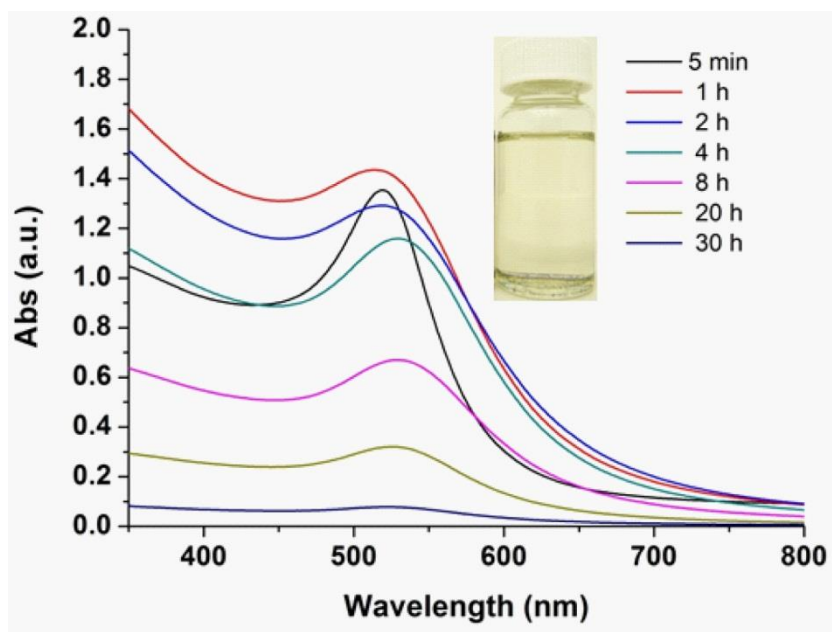
**Fig. S3** TEM image of Au NPs prepared with TOAB via BS method, the scale bar is 50 nm.



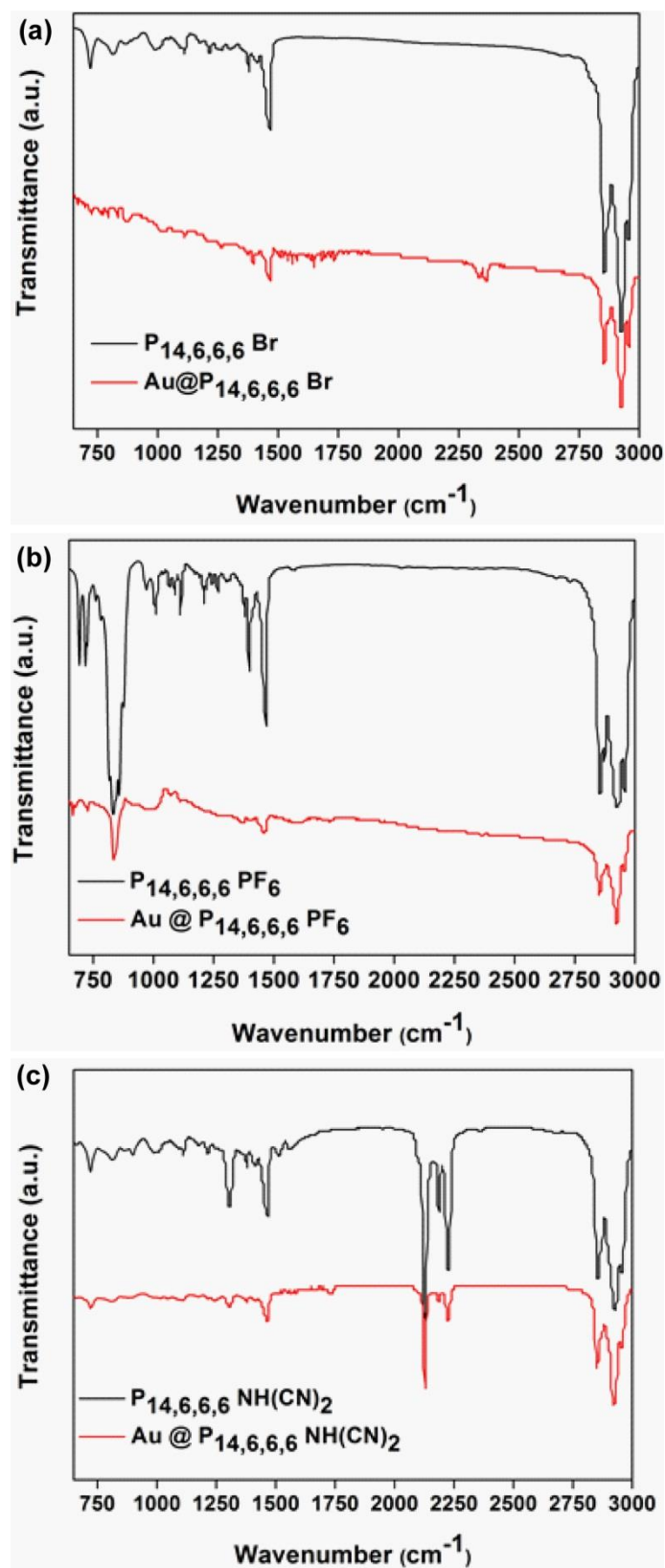
**Fig. S4** TEM image of the Au@P<sub>14,6,6,6</sub>NTf<sub>2</sub> NPs synthesized when R is 16.



**Fig. S5** UV-vis spectra of the Au@P<sub>14,6,6,6</sub>NTf<sub>2</sub>, Au@P<sub>14,6,6,6</sub>Br, Au@P<sub>14,6,6,6</sub>PF<sub>6</sub>, and Au@P<sub>14,6,6,6</sub>NH(CN)<sub>2</sub> NPs.

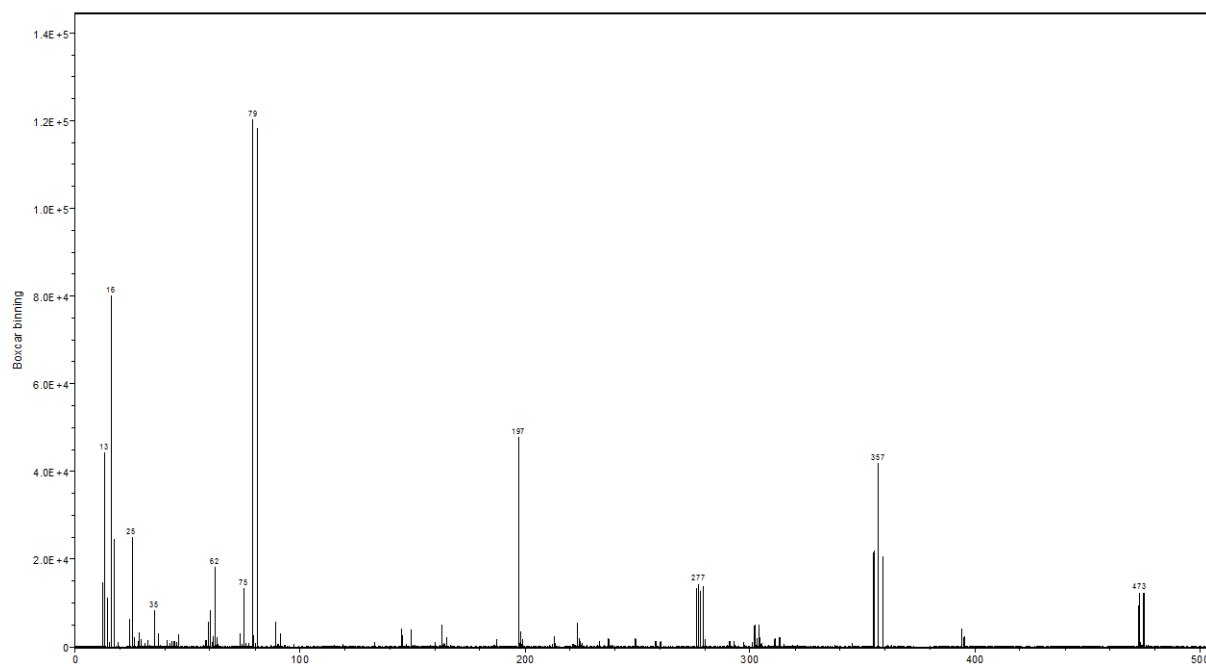


**Fig. S6** UV-Vis spectra of Au@TOAB NPs along with storage period. The particles precipitated out after 30 h.



**Fig. S7** FTIR spectra of (a)  $\text{Au@P}_{14,6,6,6} \text{Br}$  NPs and pure  $\text{P}_{14,6,6,6} \text{Br}$ , (b)  $\text{Au@P}_{14,6,6,6} \text{PF}_6$  and pure  $\text{P}_{14,6,6,6} \text{PF}_6$  and (c)  $\text{Au@P}_{14,6,6,6} \text{NH}(\text{CN})_2$  NPs and pure  $\text{P}_{14,6,6,6} \text{NH}(\text{CN})_2$ .






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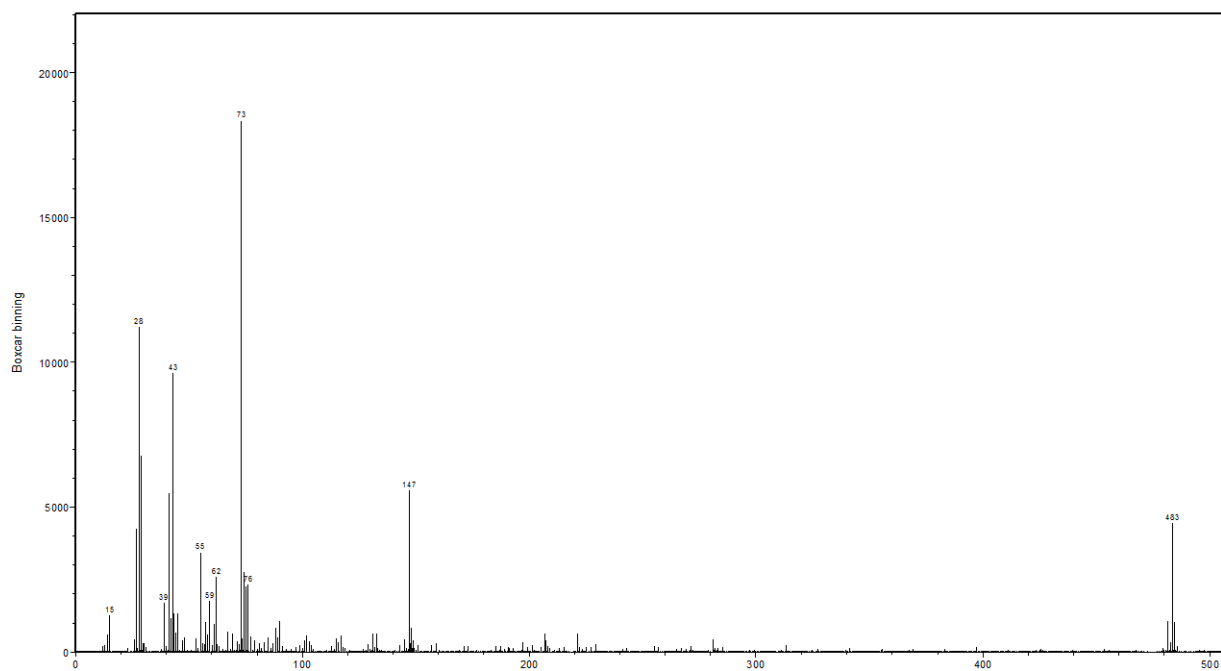
<b>m/z</b>	13	16	19	35,37	145	232,277	197	397~485
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<b>Main Ions</b>	CH <sup>-</sup>	O <sup>-</sup>	F <sup>-</sup>	<sup>35</sup> Cl <sup>-</sup> , <sup>37</sup> Cl <sup>-</sup>	PF <sub>6</sub> <sup>-</sup>	Au <sup>+</sup> Cl <sup>-</sup> , AuCl <sub>2</sub> <sup>-</sup>	Au <sup>-</sup>	C <sub>n</sub> H <sub>2n+2</sub> P (M <sup>+</sup> )
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**Fig. S8** ToF-SIMS spectrum and identification of the characteristic peaks of Au@P<sub>14,6,6,6</sub>PF<sub>6</sub> NPs.



<b>m/z</b>	13	1 6	25	46	79, 81	19 7	276~27 9	302, 304	338, 340	397~48 5
<b>Main Ions</b>	CH	O	C <sub>2</sub> H	CH <sub>3</sub> P	<sup>79</sup> Br <sup>-</sup> , <sup>81</sup> Br <sup>-</sup>	Au	AuBrH <sub>2</sub> <sup>-</sup> , AuBrH <sub>3</sub> <sup>-</sup>	C <sub>2</sub> H <sub>2</sub> AuBr <sup>-</sup> , C <sub>2</sub> H <sub>4</sub> AuBr <sup>-</sup>	C <sub>5</sub> H <sub>2</sub> AuBr <sup>-</sup> , C <sub>5</sub> H <sub>4</sub> AuBr <sup>-</sup>	C <sub>n</sub> H <sub>2n+2</sub> <sup>+</sup> P (M <sup>+</sup> )

**Fig. S9** ToF-SIMS spectrum and identification of the characteristic peaks of Au@P<sub>14,6,6,6</sub>Br NPs.